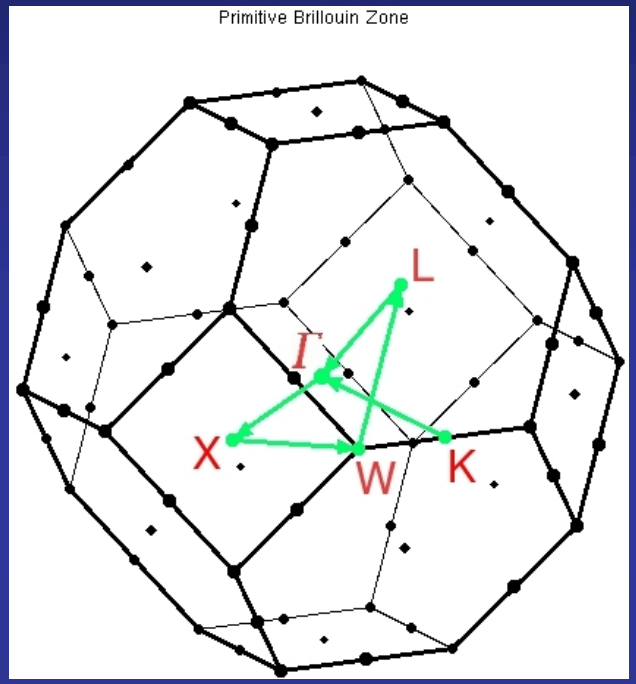
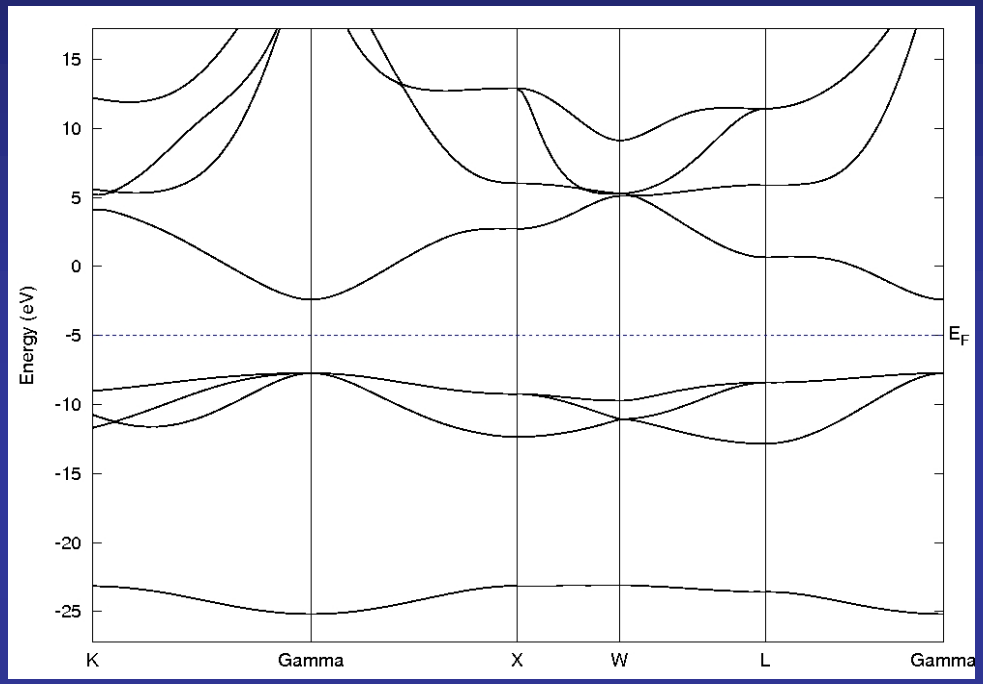
Band structure of an ionic solid: The case of MgO





Objectives

- Compute and analyze the band structure of an ionic solid

MgO an ionic solid that crystallizes in the rocksalt structure

Go to the directory where the exercise of the bands of MgO is included
Inspect the input file, MgO.fdf

```
SystemName Magnesium Oxide Crystal
SystemLabel              MgO

NumberOfAtoms            2
NumberOfSpecies          2

%block Chemical_Species_Label
  1   12   Mg
  2    8    0
%endblock Chemical_Species_Label

LatticeConstant     4.117 Ang
%block LatticeVectors
  0.000  0.500  0.500
  0.500  0.000  0.500
  0.500  0.500  0.000
%endblock LatticeVectors

AtomicCoordinatesFormat Fractional
%block AtomicCoordinatesAndAtomicSpecies
  0.000  0.000  0.000   1
  0.500  0.500  0.500   2
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  6  0  0  0.5
  0  6  0  0.5
  0  0  6  0.5
%endblock kgrid_Monkhorst_Pack
```

More information at the Siesta web page http://www.icmab.es/siesta and follow the link Documentations, Manual

The equilibrium lattice constant within LDA has been computed for you…

Rocksalt structure:

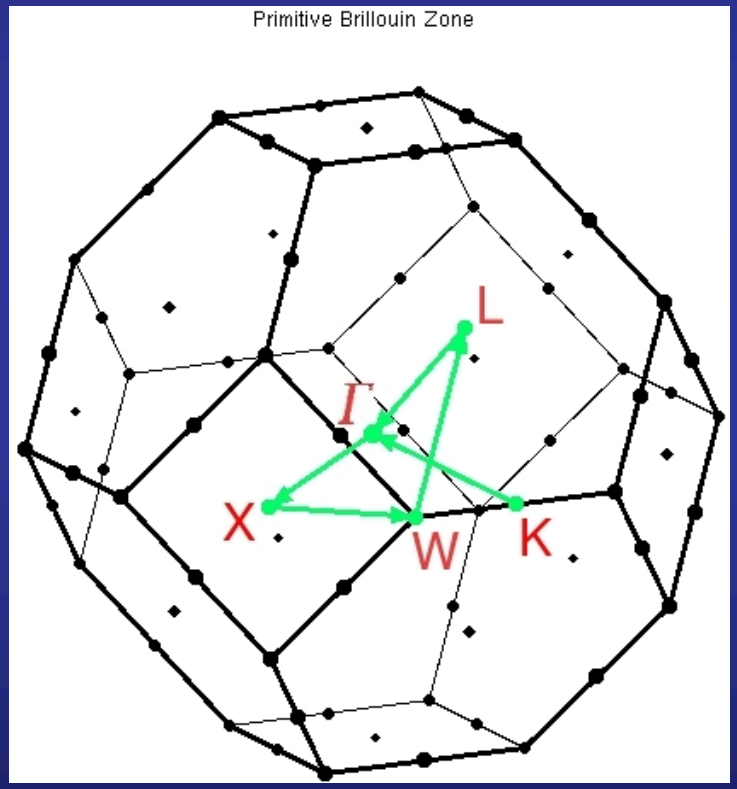
FCC lattice

+ a basis of two atoms

Sampling in k in the first Brillouin zone to achieve self-consistency

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

First-Brillouin zone of a FCC , with the high symmetry points



New variables to plot the band structure

```
BandLinesScale        pi/a
%block BandLines
1   1.5   1.5   0.0   K              # Begin at K
38  0.0   0.0   0.0   \Gamma         # 38 points from K to Gamma
36  0.0   2.0   0.0   X              # 36 points from Gamma to X
18  1.0   2.0   0.0   W              # 18 points from X to W
26  1.0   1.0   1.0   L              # 26 points from W to L
31  0.0   0.0   0.0   \Gamma         # 31 points from L to Gamma
%endblock BandLines
```

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

Check that you have all the required files

A pseudopotential file (.vps or .psf) for every atomic specie included in the input file

For Mg and O within LDA, you can download it from the Siesta web page.

Run the code,

siesta < MgO.fdf > MgO.out

Wait for a few seconds… and then you should have an output, and a file called MgO.bands

If you inspect this file, you will find something like

```
-5.01887068217278
0.000000000000000E+000    3.33847877261664
-25.1877901161284         143.069317296392
        18            1           150
0.000000    -23.1506    -11.6755    -10.7473     -9.0169      4.0923 ...
...
```

Energy of the Fermi level

Minimum and maximum length of the path in k-space

Minimum and maximum eigenvalues

Number of orbitals in the unit cell, number of different spin polarization, and number of k-points in the walk through the 1BZ

Coordinate of the k-point in the path, and eigenvalues (in eV). There are as many eigenvalues as orbitals in the unit cell.

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone

To plot the band structure, there is a Utility in the directory Util, called gnubands.f

To use it:

```
$ cd <your_siesta_path>/Util/Bands
$ make OBJDIR=Obj/
```

(where OBJDIR should point to the directory where the arch.make you want to use is)

In this exercise, we also provide the fortran file for you. Just type:

```
<your_fortran_compiler> -o gnubands.x gnubands.f
gnubands.x < MgO.bands > MgO.bands.gnuplot.dat
```

The name of this file is free

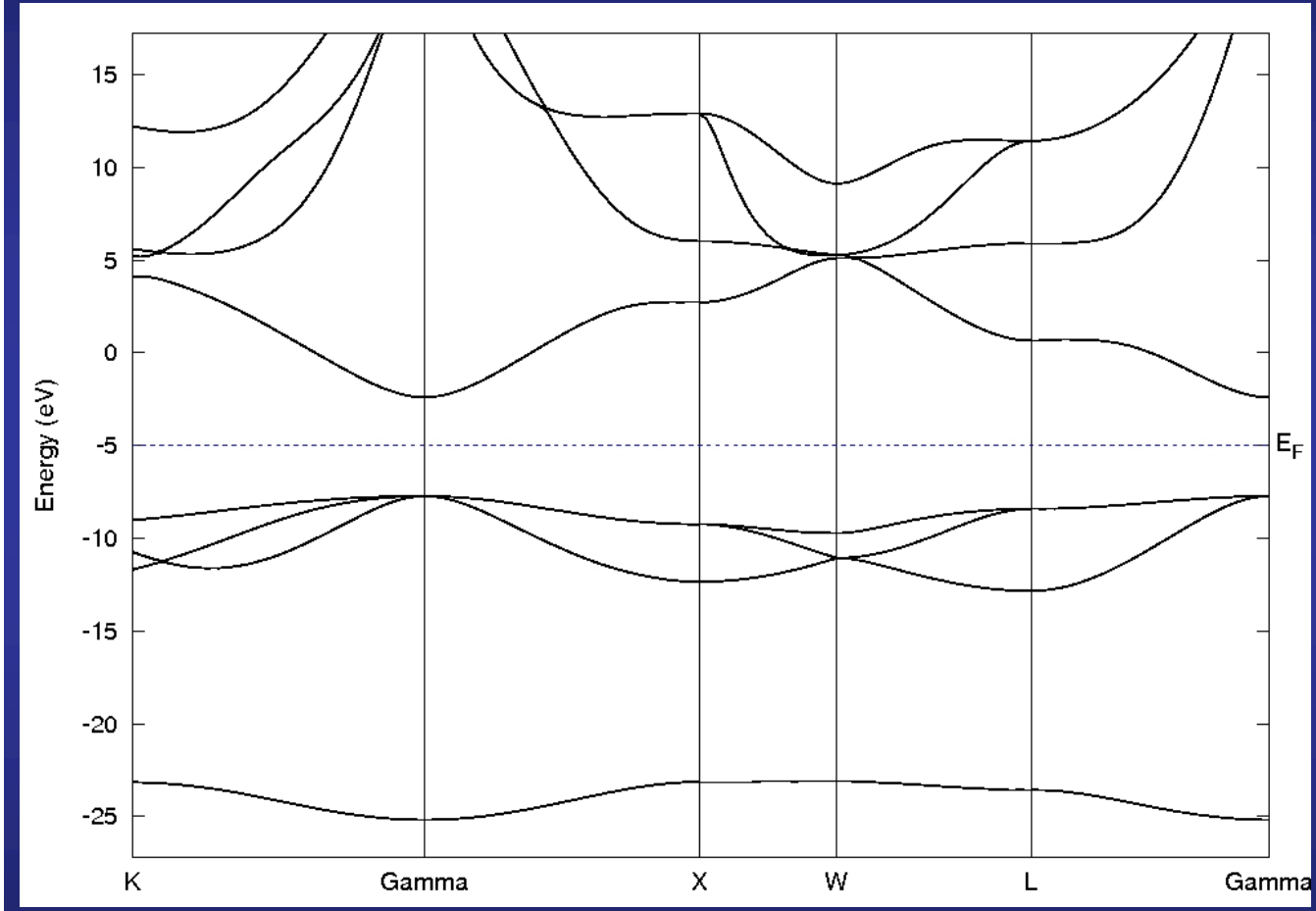
```
gnuplot
plot "MgO.bands.gnuplot.dat" using 1:2 with lines
```

set xrange [0:3.34] → 3.34 is the position of the last k-point in the path in k-space

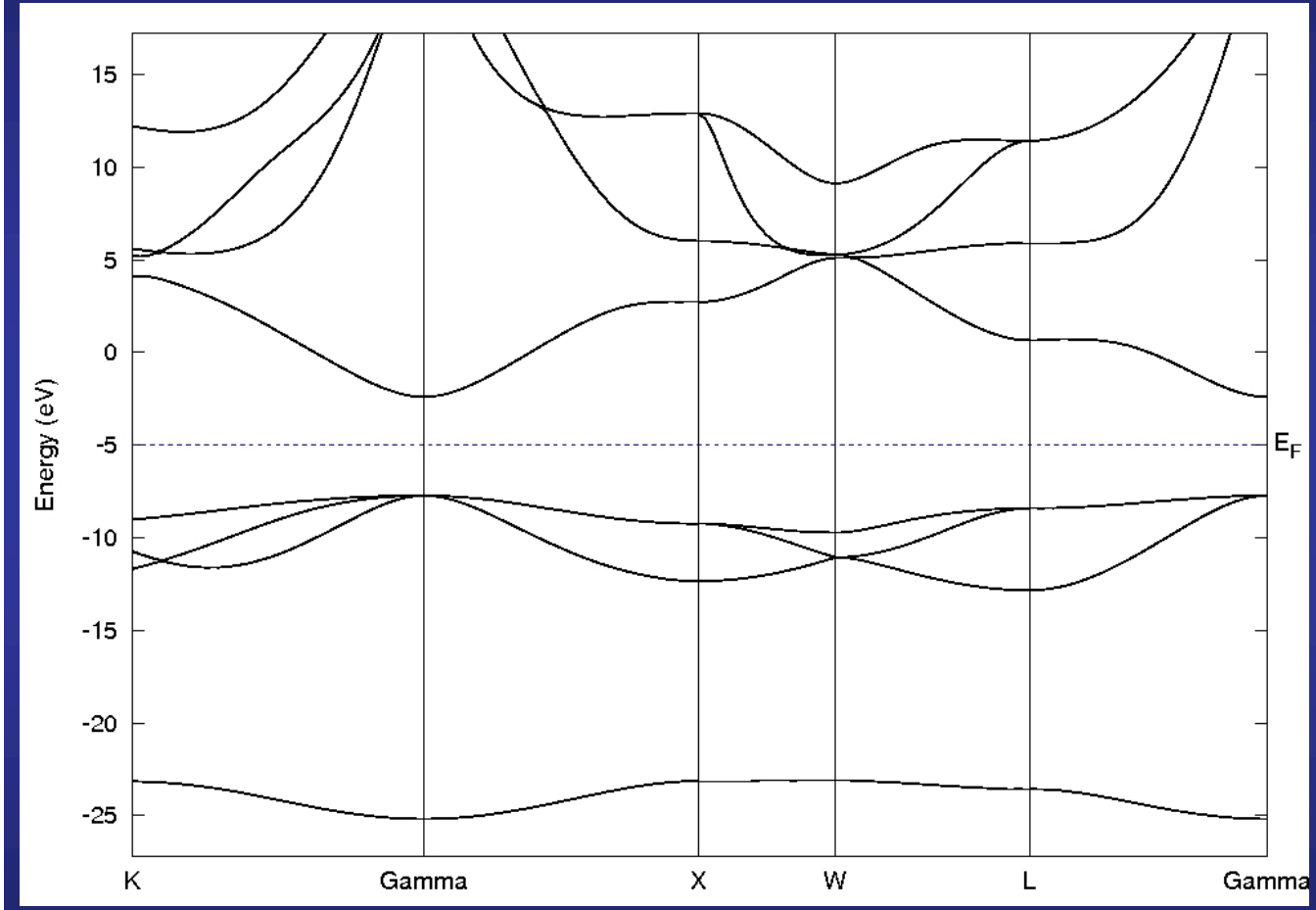
set yrange [-30.0:25.0] → this is large enough to include all the valence bands

```
replot
```

Once SCF has been achieved, we compute the bands along the high symmetry points in the First-Brillouin zone



The most important point: analyze your results



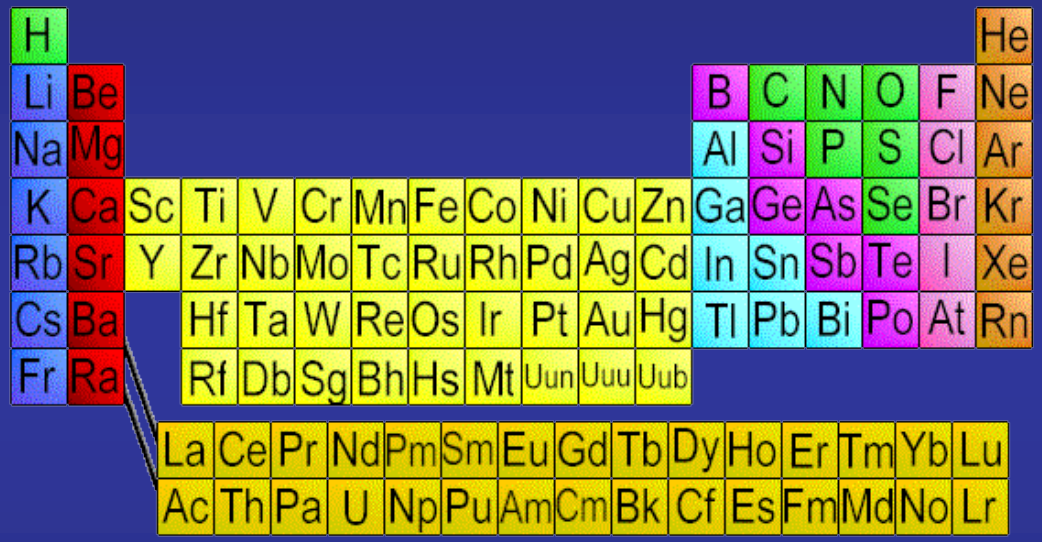
The Fermi energy lies in a gap ⇒ insulator

Theo. direct gap = 5.3 eV

Expt. Gap = 7.8 eV

(LDA band gap understimation)

The most important point: analyze your results



Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ → Mg^{2+}

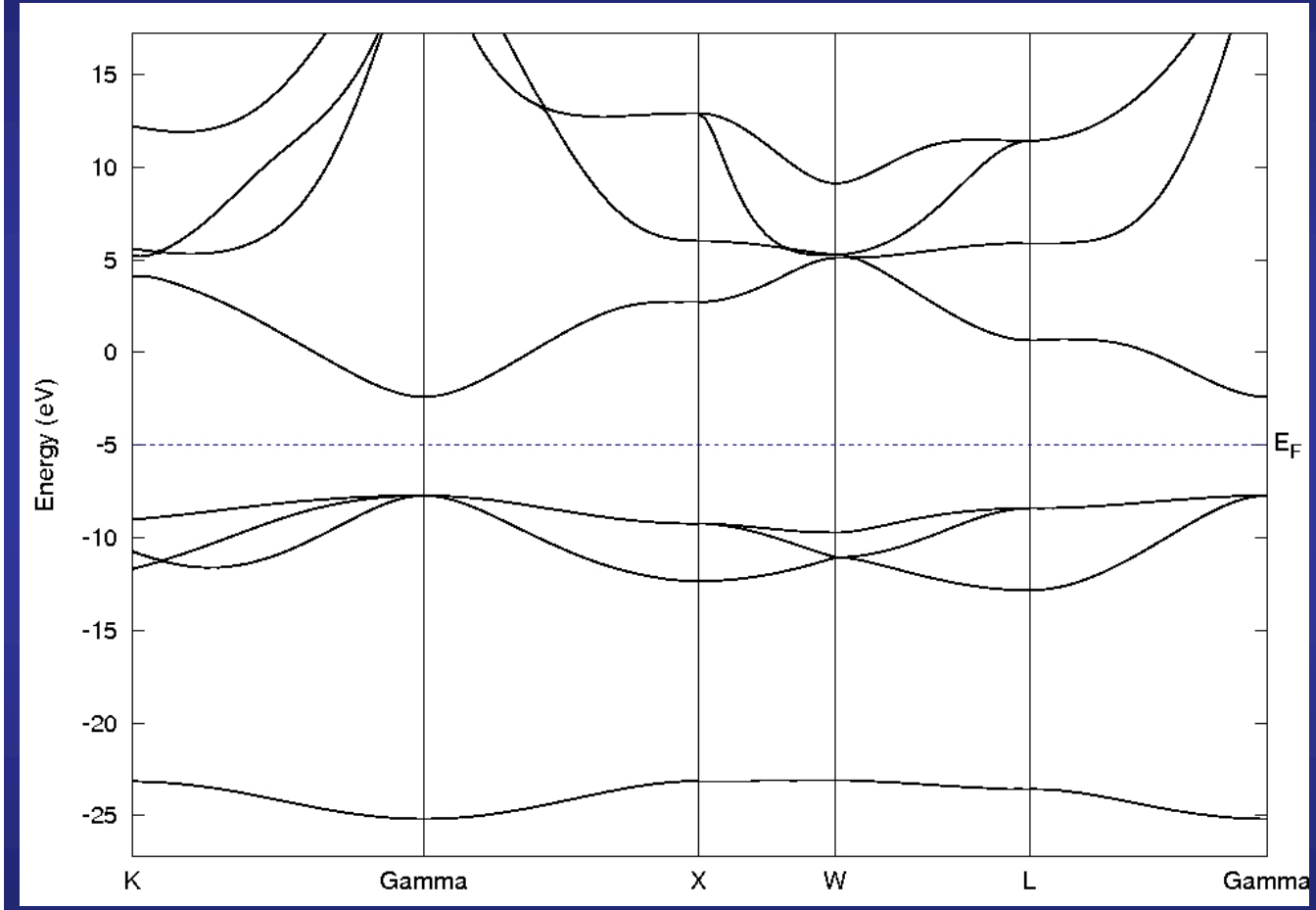
Mg loses two electrons

that are gained by O

O: $1s^2\ 2s^2\ 2p^6$ → O^{2-}

One would expect O (one *s* band and three *p* bands) bands completely full and Mg bands completely empty

The most important point: analyze your results



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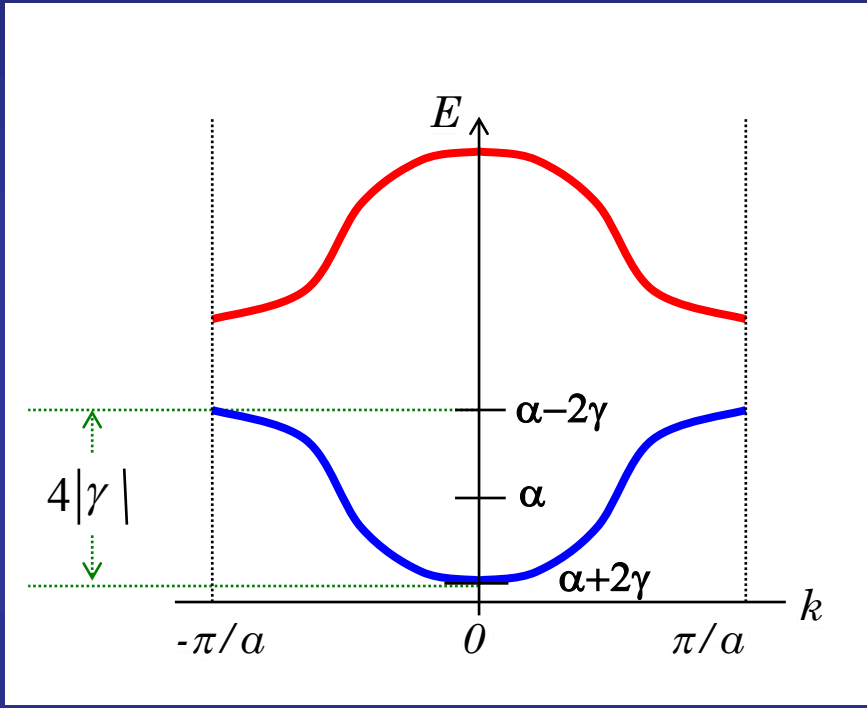
(LDA band gap understimation)

O 2*p*

(three bands)

O 2*s*

Once the transfer of charge is produced, the atoms only interact electrostatically

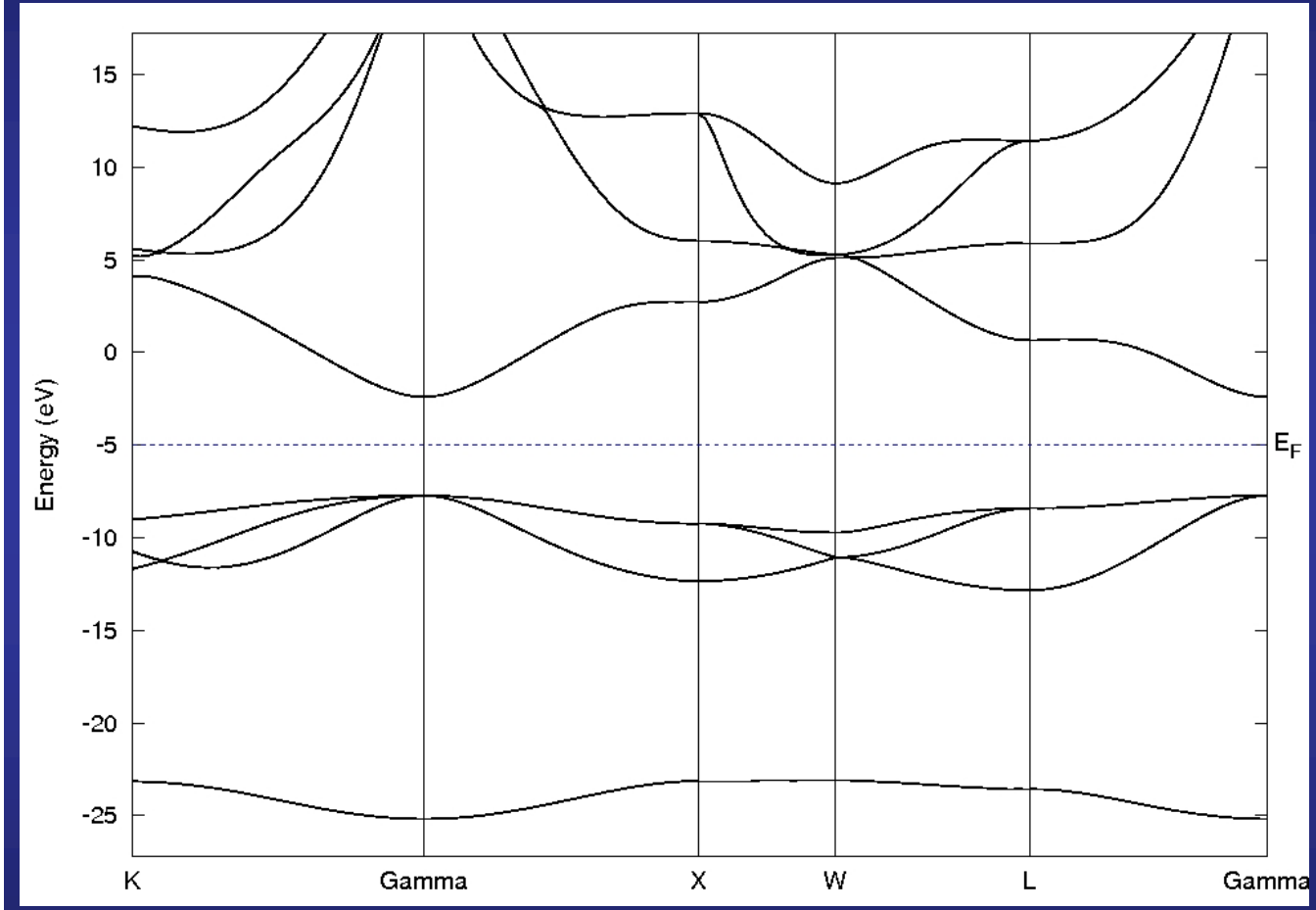


In a very simplified tight-binding model,

the width of the band is proportional to the interactions with nearest neighbours

If the interaction is small, the bands are very flat.

The most important point: analyze your results



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(LDA band gap understimation)

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O 2*s*

Very small disperion of the O *s* and O *p* bands